

Chemical composition and mass size distribution of fine particulate matter emitted by a small masonry heater

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Residential wood combustion is a significant particulate emission source in many European countries. Especially for fine particle emissions in wood combustions, the lacking knowledge of emission factors (F_E) makes assessment of their contribution to ambient concentrations difficult. One reason for the discrepancy between modeled and measured contributions is many variables involved in combustion process. In this study, the fine particulate matter (PM) emissions coming from batch combustion of birch wood in a small masonry heater were investigated. The experiments were carried out in the specified conditions (normal and smouldering combustion, NC and SC, respectively). To enable various chemical analytical techniques, two sampling combinations for $PM_{2.5}$ (particle diameter $< 2.5 \mu m$), and size-segregated sampling were used. The samples were analyzed for gravimetric mass, major ions, monosaccharide anhydrides (MA, including levoglucosan, galactosan and mannosan), trace elements, elemental carbon (EC) and water-insoluble and -soluble particulate organic matter (WISPOM and WSPOM, respectively). F_E of $PM_{2.5}$ based on gravimetric mass was three times higher for SC than for NC. Particulate organic matter ($POM = 1.6 \times OC$) accounted for approximately 30% and 70% of F_E of $PM_{2.5}$ in NC and SC, respectively. The corresponding values for EC were 32% and 25%. About 30% of the OC was water-soluble. Ions constituted about 20% of the F_E of $PM_{2.5}$ in NC but only a few percents in SC. Potassium comprised around 60% of the analyzed ions. The fraction of trace elements consisting 94% of Zn was only about 1% of the total $PM_{2.5}$ emissions. This study showed strong influence of combustion practice on emissions of the major chemical components from the small-scale wood combustion.

Introduction

Particulate emissions originating from residential wood combustion are significant in many European countries, especially during wintertime (Pio *et al.* 2007, Simpson *et al.* 2007, Tsyro *et al.* 2007). Also in Finland, a substantial number of households use firewood as a fuel either in their primary or secondary heating systems. There are approximately 2.2 million fireplaces, masonry heaters, ovens and boilers using wood as fuel in Finland (Haaparanta *et al.* 2003). In addition, wood is used in about 1.5 million sauna stoves.

During the heating season 2000–2001 in Finland, wood comprised about 40% of the total heating energy consumed in residential houses, farms and summer houses (Peltola 2005). This is about 13% of the total annual heating energy (Statistics Finland 2001). The most important firewood type is birch constituting about one third of all raw wood used for the heating (Peltola 2005). The most common way to use wood in residential heating is combustion of wood in few-kilogram batches.

Heating with wood is common even in the Helsinki metropolitan area, where about one fifth of the Finnish population, over one million, lives. Due to good availability of district heating, only about 3% of the households in the Helsinki metropolitan area uses wood for primary heating, but it is more common to use wood for secondary heating (Luoma 1997, Statistics Finland 2002, Haaparanta *et al.* 2003).

The use of biomass energy in households is encouraged by the Finnish government. The Ministry of Trade and Industry published a program in 1999 aiming to reduce carbon dioxide emissions. According to the program, the use of renewable energy should be increased by 60% from the year 2001 to 2025. By 2025, the amount of wood burned by households should exceed that in 2001 by almost 30% (Eskola *et al.* 2003). The use of wood fuel is considered neutral with regard to greenhouse gas emissions. However, without substantial improvement of combustion techniques, the increase of small-scale wood burning would certainly increase particulate emissions and impair local air quality.

In Finland, several kinds of heat retentive and non-retentive heaters and sauna stoves are used.

In a typical Finnish masonry heater, the energy released is efficiently stored in the large mass of the heater. This is in contrast to the lightweight metal stoves often used in central Europe and in Scandinavian countries. These stoves operate at a low combustion rate leading to long operation times at low power. Also, in contrast to open fireplaces, which are common in the US, and cookstoves in developing countries, in the Finnish appliances wood is burnt in a closed firebox and the combustion air is controlled (Tissari *et al.* 2007). The way how wood is burnt and wood quality have a great influence on emissions of particulate matter in the small-scale wood combustion. Moisture of firewood, volume of combustion air, combustion temperature as well as the log and batch size contribute to the combustion efficiency. For example, overloading the firebox, insufficient air supply and poor fuel quality (e.g. wet wood) will create conditions for incomplete combustion (Johansson *et al.* 2004, Tissari *et al.* 2007). Depending on the combustion technology and heating habits, different amounts of fine particles (particulate matter with particle diameter $< 2.5 \mu\text{m}$, $\text{PM}_{2.5}$) and other pollutants are produced. It has been estimated that in the year 2000 about 25% of the total annual $\text{PM}_{2.5}$ emissions in Finland originated from small-scale wood combustion (Karvosenoja *et al.* 2008). The emitted $\text{PM}_{2.5}$ from wood combustion is composed mainly of ash, condensed organic material and soot. Emission height is usually just a few meters above the ground level. Thus, particulate emissions do not have much time to dilute, oxidize or react chemically before affecting people. During the heating season, the cold days are often also collocated with poor mixing due to atmospheric stability and low atmospheric boundary layer. Health studies in residential areas with the prevalent small-scale wood combustion have indicated that asthmatic subjects are vulnerable to this kind of air pollution (Larson and Koenig 1994, Boman *et al.* 2003). There are also studies that show an association between fine particulate pollutions (not only wood combustion) and cardiovascular diseases but evidences supporting this association are still quite weak (Pekkanen *et al.* 2002, Boman *et al.* 2003, Pope *et al.* 2004).

Some chemical compounds, such as OC, EC, levoglucosan, potassium and zinc, are known

to be tracers of wood smoke in the atmosphere (e.g. Simoneit *et al.* 1999, Hedberg *et al.* 2002, Zdráhal *et al.* 2002). In atmospheric aerosol measurements, the contribution of POM to PM is observed to be clearly elevated when air masses are influenced by biomass burning (e.g. Khalil and Rasmussen 2003, Saarikoski *et al.* 2008b). The EC-to-OC ratio can also be used to assess the source contributions to PM. A low EC-to-OC ratio usually indicates biomass burning in the atmosphere (e.g. Khalil and Rasmussen 2003). In addition, the EC-to-OC ratio can also be used as an indicator of the burning temperature because the formation of soot increases at high temperatures (Khalil and Rasmussen 2003). The atmospheric mass concentrations of levoglucosan in Finland have been reported to be typically some tens of ng m^{-3} (Sillanpää *et al.* 2005b, 2006). Ambient air influenced by biomass combustion, such as residential wood burning or wild fires, have been found to have more than ten times higher levoglucosan concentrations (Zdráhal *et al.* 2002, Sillanpää *et al.* 2005b, Yttri *et al.* 2005, Jordan *et al.* 2006, Saarikoski *et al.* 2008b). Also the higher contribution of levoglucosan to OC in ambient air indicates the influence of wood combustion (Zdráhal *et al.* 2002, Yttri *et al.* 2005). Increased ambient concentrations of potassium and zinc have also been reported in connection with wood combustion or biomass burning (e.g. Hedberg *et al.* 2002, Saarikoski *et al.* 2008b). For example, according to Saarikoski *et al.* (2008b), the mass concentration of K^+ was approximately seven times higher during wildfire episode when compared with the normal urban background concentrations. In the contribution of trace elements from different sources, Zn has been observed to comprise approximately 1% in background, 0.4% in traffic tunnel and 13% in wood burning (Hedberg *et al.* 2002).

The objective of the present study was to investigate emission factors of a typical masonry heater used in Finland. The influence of different combustion conditions to the PM emissions and to mass size distributions of different chemical components were studied. A commonly used small masonry heater was used at two different burning conditions corresponding to a normal (flaming) and smouldering ways to burn wood. Birch was used as firewood. Combustion condi-

tions were changed by controlling the air supply and using different wood log and batch sizes.

Experimental setup

Masonry heaters are commonly used for the secondary heating and pleasure especially in the new residential houses. A common type of the small Finnish masonry heaters was used in this study. A special attention was paid to the influence of the operating conditions on particulate emissions. Birch wood was used as fuel. The particulate emissions were measured in the dilution tunnel. Temperatures and dilution ratios (DR) in the tunnel were controlled and measured.

Combustion and dilution setup

A commercially-available, small soapstone masonry heater was used in the experiments. The heater uses a conventional combustion technique with a grate in firebox for the main air supply. The burn rate is controlled by the main air supply through the ash box below the firebox grate. Birch logs were used as firewood and the fuel mass flow rate was measured by keeping the masonry heater on a balance. Two different combustion conditions were created. Five measurements were made using conditions called the normal combustion (NC) and three corresponding to the smouldering combustion (SC). The NC was characterized by the best operational practice of this heater, whereas the SC corresponded to the slow heating combustion that results from the common user mistakes in operational practice (overloading the firebox, restricting air supply to prolong heating). The interest of this study was to characterize how different combustion conditions affect the particulate emissions and mass size distributions of chemical components. If the batch size is optimal, arrangement of birch logs is compact and combustion air supply is sufficient, the burning temperature rises and gasification of wood is suitable. This makes the combustion process relatively good, and is here called the normal combustion (NC).

Both combustion procedures started with a similar ignition/kindling batch, 1.7 kg of wood

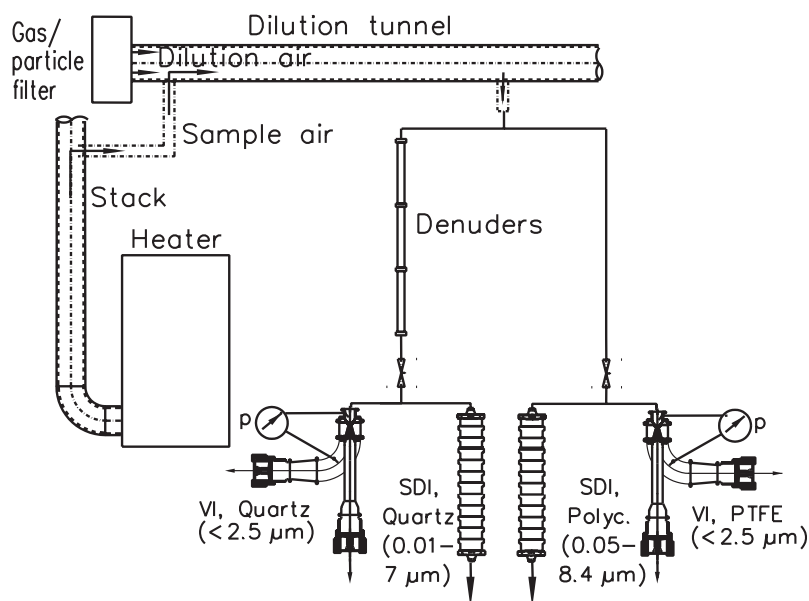


Fig. 1. Schematic picture of the experimental setup.

log and 0.15 kg of wood sticks with a minor amount of birch bark. Fifteen minutes after the ignition, the kindling batch was followed by two to three subsequent batch additions. In the NC procedure, three batches (2.4 ± 0.1 kg batch⁻¹) were added approximately every 20 minutes. When the batch size was increased (3.5 ± 0.1 kg batch⁻¹) and the log arrangement changed to be more fragmented, in addition to the inadequate combustion air supply and the longer batch burning duration (30 minutes), the combustion was incomplete (smouldering combustion, SC). The experiments excluding the combustion of burn out residues lasted for 75 to 85 minutes. Only one experiment per day was possible, because the heater had to be cooled down before each subsequent experiment to keep the conditions constant.

The fuel flow rate, stack pressure and temperature of combustion gases were measured continuously. In addition, concentrations of different combustion gases, such as organic gaseous carbon compounds (OGC), NO, NO₂, CO, CO₂ and O₂, were measured and recorded. The combustion air from the stack was first diluted in a dilution tunnel according to the ISO 8178-1 standard (Sippula *et al.* 2007). The dilution was done with dry, particle-free air. Also nitrogen oxides and hydrocarbons were filtered from the dilution air. The dilution ratio varied between

180 and 330 with an average value of 214. The temperature in the tunnel was on average 24 °C. A similar experimental setup has been described by Sippula *et al.* (2007).

The fine particle sampling was made from the dilution tunnel (Fig. 1). By collecting the samples at the temperature of the dilution tunnel (24 °C), it was assumed that the composition of particulate matter corresponded better to fine particles immediately after they had been emitted to ambient air from a small-scale wood combustion appliance.

Particulate matter sampling and analysis

The sampling setup of this study was designed to reveal differences in particulate matter emissions between the NC and the SC (Fig. 1). The chemical composition of the PM_{2.5} and chemical particle size distributions were measured. The sampling after the dilution tunnel was made using two small deposit area impactors (SDI; Maenhaut *et al.* 1996) with a nominal particle size range of 0.045–8.5 μm for thin film substrates, and of 0.015–6.7 μm for quartz fiber substrates (Maenhaut *et al.* 1996, Saarikoski *et al.* 2008a). The SDI segregates the particle sample into 12 size classes, allowing the measurement of a chemical mass size distribution. In parallel

with the SDI, two virtual impactors (VI; Loo and Cork 1988) with a 50% cut-off point at $2.5\ \mu\text{m}$ (aerodynamic diameter) were used to collect the $\text{PM}_{2.5}$ samples for the analysis of the chemical composition.

The first set of the measurements consisted of sampling by using the parallel VI and SDI with 47-mm polytetrafluoroethylene (PTFE) filters (Millipore, $3.0\ \mu\text{m}$, FSLW04700) and 21-mm punched polycarbonate substrates (poreless polycarbonate films from Nuclepore, thickness $10\ \mu\text{m}$), respectively. The polycarbonate substrates were coated with Apiezon L-vacuum grease to reduce the particle bounce. The PTFE filters were analyzed gravimetrically before and after the sampling (Mettler M3-microbalance, Mettler Instrumente AG, Zurich, Switzerland). The handling and weighing of the PTFE filters as well as the chemical analyses of the particulate matter collected on them have been described in detail elsewhere (Sillanpää *et al.* 2005a, 2006). Major ions were analyzed using ion chromatography (IC), while levoglucosan, galactosan and mannosan (monosaccharide anhydrides, MA) were analyzed by using a liquid chromatograph coupled to an ion trap mass spectrometer (LC-MS), and trace elements were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Major ions and the MA were analyzed also from the SDI polycarbonate substrates.

The second set of the measurements was conducted by using a combination of the VI and the SDI with three annular denuders (URG-2000, $30 \times 242\ \text{mm}$, Chapel Hill, NC) upstream of the sample flow. The denuders were coated with XAD-4 material according to Gundel *et al.* (1995) to remove interfering organic vapors. Quartz filters (Whatman, QM-A, $47\ \text{mm}$) for the VI were purified by keeping them at $550\ ^\circ\text{C}$ for approximately five hours. The filters were used for organic (OC), elemental (EC) and water-soluble organic (WSOC) carbon. The water-insoluble organic carbon (WISOC) was calculated by subtracting the analyzed WSOC from the analyzed OC. In the VI, a backup filter was used to measure the positive artefact caused by organic vapors. Quartz fiber substrates for the SDI (diameter $21\ \text{mm}$) were punched from a quartz filter sheet (Whatman, QM-A) and the punched substrates were purified like the VI

filters. The denuders were changed 15 minutes after the combustion begun because of high concentrations of organic vapors in the beginning of the burning cycle. Also the VI samples with quartz filters were changed. During the change also the impactor sampling was interrupted. The air flow through the VI ($16.7\ \text{l min}^{-1}$) was controlled by using a rotameter and differential pressure gauge. The last stage in the SDI acts as a critical orifice that sets the flow through the equipment constant ($11.45\ \text{l min}^{-1}$) and a flow rate control is not needed.

Organic and elemental carbon (OC and EC)

Organic and elemental carbon were determined with a thermal-optical carbon analyzer (TOA; Sunset Laboratory Inc., Oregon; Birch and Cary 1996). A 1.5-cm^2 piece was cut from the VI quartz filter for the analysis. The sampling area in the SDI is smaller than $1.0\ \text{cm}^2$ and therefore the whole deposit area can be analyzed. The operation principle of the thermal-optical analyzer is in short the following: OC is volatilized at four subsequent temperature steps in pure helium atmosphere, after which the EC is determined in a mixture of oxygen and helium (2% oxygen) at six temperature steps. An optical correction is applied for the separation of pyrolysed OC from EC. The used temperature program was similar to the NIOSH program, except for the last temperature step in helium phase that was decreased from 850 to $800\ ^\circ\text{C}$. Inorganic carbon (carbonate carbon) can interfere with the determination of OC, since it volatilizes concurrently with the OC in the helium phase. However, on the basis of the thermograms, no carbonate carbon was detected in this study.

A ratio between the molecular weight of different organic compounds and carbon weight in the wood smoke is needed to convert OC to particulate organic matter (POM). Turpin and Lim (2001) suggested that lowest value for this scale factor should be in range of $1.4\text{--}1.8$ and $1.9\text{--}2.3$ in urban and non-urban (aged) environments, respectively. In this study the factor 1.6 was used, because the dilution alone was not thought to cause further oxidation of particulate matter as is the case during aging in the atmosphere.

Water-soluble organic carbon (WSOC)

The WSOC analyses were done by using a TOC-V_{CPH} organic carbon analyzer (Shimadzu) with a highly sensitive catalyst. A 2-cm² piece was cut from the PM_{2.5} filter for the WSOC analysis. The sample was submerged into 15 ml of deionized water and rotated for 15 minutes prior to the analysis. A non-purgeable organic carbon (NPOC) method was used. In the NPOC method the sample is first put into 15 ml of deionized water to extract all water-soluble organic carbon from the filter. Thereafter, the sample solution is drawn through a plastic tube to the syringe using an 8-way valve. Addition of acid (1% 2 M HCl) and helium bubbling (1.5 minutes) are done in the syringe. After that, all inorganic carbon should be converted into carbon dioxide and should be evaporated from the sample solution. After bubbling, the sample is injected into an oven, where it is catalytically oxidized to carbon dioxide at 680 °C. The used injection volume was 500 μ l.

The detection limit for the TOC-V_{CPH} is 4 μ g l⁻¹ and the standard deviation for the repeated measurements is less than 1.5% (values given by the manufacturer). The measurement error resulting from the TC content in the water used to make the solutions and in the blank filters is typically much greater than error resulting from the system blank value. The estimated error of the measurements is 15% for atmospheric concentrations < 2 μ g m⁻³ and 10% for concentrations > 2 μ g m⁻³.

In addition, the analyzed WSOC mass concentrations were converted to water-soluble particulate organic matter (WSPOM) by multiplying the WSOC mass concentrations by a factor of 1.8.

Monosaccharide anhydrides (MA)

MA (levoglucosan and its isomeric compounds galactosan and mannosan) that are degradation products of cellulose and hemicelluloses were analyzed with a liquid chromatograph coupled with an ion trap mass spectrometer (LC-MS, Agilent Technologies SL). One quarter of a VI-PTFE filter sample was extracted with a 5-ml

mixture of tetrahydrofuran and water (1:1) in the ultrasonic bath for 30 minutes. In this study, a LC-MS method was used with deionized water (Milli-Q, Millipore Gradient A10) as an eluent at a flow rate of 0.1 ml min⁻¹. Two LC columns (Atlantis, dC₁₈ 3 μ m, 2.1 \times 150 mm, Waters) were used at 7 °C. The ionization technique was electrospray and the monitored ion was m/z 161. Except the extraction, the analytical procedure was similar for the SDI samples. For the SDI samples, same sample solution was used in both the LC-MS and IC analyses, because of the small sample size. Thus, polycarbonate substrates from each of the SDI stages were first wetted with methanol. Thereafter, the solution was diluted to 5 ml with Milli-Q water. This solution included 10% of methanol. The resolution in the LC was insufficient to separate the three MAs from each other when analyzing the SDI samples. Thus, the SDI results will be reported as the sum of the MA whereas MA analyzed from the VI-PTFE filters will be reported separately for each of the three compounds. The uncertainty of the LC-MS method used for the MA analysis from the VI samples was estimated to be 20%. The uncertainty for the SDI samples was higher, because of the smaller sample size and different extraction method.

Major ions

The concentrations of sodium (Na⁺), ammonium (NH₄⁺), potassium (K⁺), magnesium (Mg²⁺), calcium (Ca²⁺), chloride (Cl⁻), nitrite (NO₂⁻), nitrate (NO₃⁻), sulfate (SO₄²⁻) and oxalate were determined from the PTFE filters and polycarbonate substrates using two ion chromatographs (Dionex DX500). One quarter of a PTFE filter was first wetted with 500 μ l of methanol for effective extraction of the collected particulate matter. The samples were subsequently diluted to 10 ml with deionized water (Milli-Q, Millipore Gradient A10) and extracted for about 10 minutes. The anions were analyzed using a 4 \times 250 mm-AS-11 analytical column, a 4 \times 50-mm AG-11 guard column with the chemical suppression (sulfuric acid) and NaOH eluent. The cations were analyzed using a 4 \times 250-mm CS-12A analytical column, a 4 \times 50-mm

CG-12A guard column, a 4-mm CSRS-ULTRA II suppressor and methanesulfonic acid eluent. The same procedure was used for extraction and analysis of each of the SDI stages, except the extraction volume that was 5 ml. Uncertainties in the IC analyses have been estimated to be around 10% (Teinilä *et al.* 2000). A fraction of the solution was used to determine the MA mass size distribution with the LC-MS as described in the previous section.

Trace elements

Trace elements were analyzed using inductively coupled plasma mass spectrometer (ICP-MS; PerkinElmer Sciex Elan 6000, The PerkinElmer Corporation, Norwalk, USA) for a quarter of the VI-PTFE filter samples. The aerosol sample was extracted with a HNO_3 -HF mixture (3:1) (Jalkanen *et al.* 1996). Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, V and Zn were analyzed. The uncertainty of the ICP-MS analysis is in the order of 25% for Cr, Cu and Ni, as well as 30% for Zn, 35% for Fe and 20% for all the other trace elements.

Results and discussion

Effects of the different combustion conditions were clearly reflected in the chemical composition of particles emitted from wood burning. Oxygen content is one factor that influences the combustion efficiency and emissions. Especially during the ignition phase when fire intensity is increasing, the oxidation of volatile compounds in the interior of the flame zone can be insufficient due to inadequate air supply and too low combustion temperature (Reid and Hobbs 1998, Reid *et al.* 2005). This leads to incomplete burning with increasing particulate emissions. Incomplete burning during the ignition was the reason for changing the denuders and the VI samples with quartz filters 15 minutes after the beginning of the combustion. This time may be even too long, because the ignition period lasted only for some minutes. Thus, especially in the smouldering combustion (SC), the denuders may have been overloaded by gaseous compounds,

which would increase uncertainty in the OC and EC analysis due to the positive artifact. It is hard to assess the overloading quantitatively, but the higher OC concentration in the backup filter usually indicates either the evaporation of OC from the front filter or, in the case of overloading of the denuders, the sampling of gaseous organic compounds onto the backup filter. However, this is speculative because emissions between different combustions can vary much and there are not enough parameters monitored online to detect the possibility for the overloading. In the data handling, the mass concentrations of the analyzed compounds in the dry combustion gas were reduced to the 13% oxygen content.

Emissions from birch wood combustion contain remarkable amounts of organic compounds that have a low molecular weight-per-carbon-weight ratio (1.1–1.7), such as polycyclic aromatic hydrocarbons (PAH) and ketones (Turpin and Lim 2001, Hedberg *et al.* 2002). The scaling factor for levoglucosan is 2.3 (Turpin and Lim 2001), but it contributed only 2%–3% of the fine PM mass in this study. Taking previous facts into account, the scaling factor 1.6 was chosen to convert OC to POM. Although uncertainty is involved in this choice, it is reasonable for particulate matter coming directly from a combustion source without aging and oxidation in the atmosphere. WSOC was converted into water-soluble particulate organic matter (WSPOM) by multiplying WSOC by a factor 1.8. Turpin and Lim (2001) recommended a higher factor of 2.2–2.6 for aerosols impacted heavily by wood smoke. However, the factor used here was within the range of factors typical for water-soluble organic species, like some PAH, ketones and sugars (levoglucosan), usually occurring in wood combustion emissions (e.g. Turpin and Lim 2001). The scale factors for these species have ranged from 1.1 to 2.3 (Turpin and Lim 2001). In addition, the emissions measured here were fresh, and oxidation in the atmosphere did not yet affect the molecular-weight-to-carbon-weight ratio. Thus, the use of a rather low scale factor was reasonable but can cause slight underestimation of WSPOM emissions.

The emission factors (F_E) determined for the chemical constituents from the VI samples in the NC comprised $85\% \pm 5\%$ of the total gravimetric

emissions (Table 1). Corresponding values in the SC were 93% and 97% for the two successful measurements, respectively. The fraction of the unidentified matter could be particle-bound water or some insoluble material in ash particles, which could not be quantified. In addition, the unidentified matter could partly be explained by the choice of rather low OC-to-POM conversion factor.

Different combustion conditions of this study were reflected in the variation of the F_E values of particle emissions and ratios between different compounds. The influence of the combustion conditions was clearly seen also in the mass size distributions of different chemical compounds determined from the SDI samples. Here, the SDI results can be considered qualitative, whereas the analyses based on the VI samples were quantitative. One obvious reason for this was the extraction of the MA samples for the LC-MS analysis. The extraction of the SDI samples differed from the normally-used technique, which increased the uncertainty of the results. The F_E for POM and EC analyzed from the quartz SDI samples were normalized to the sum of the F_E of these analyzed components. In addition, ions and MA analyzed from the polycarbonate SDI samples were normalized to the sum of the F_E of ions and MA. The normalized values of F_E were further converted into correspond the logarithmic particle diameter scale by dividing the F_E of each of the SDI stages with the width of the corresponding size channel.

PM_{2.5} emissions

The F_E for the PM_{2.5} varied considerably between the NC and SC conditions. Usually within one condition, there were only reasonable variations.

However, one sample of the SC experiments differed clearly from the two other ones with regard to a smaller F_E for the PM_{2.5} but with extremely high OC emissions. The high OC emission rate was most likely due to overloading of the denuders with gas-phase compounds. Thus, the gaseous organic matter that penetrated the denuders could have been captured by the quartz filters. In this case, the OC emission may have been overestimated. Thus, only two samples of the SC were used when the F_E values for different chemical compounds were calculated. The F_E at the normal conditions (five measurements) ranged from 2.2 to 3.2 g of the PM_{2.5} per kg of wood burned with an average (\pm SD) value of 2.7 ± 0.4 g kg⁻¹ (Table 2). The corresponding range for the SC (two measurements) was 8.7–9.0 g kg⁻¹ that was approximately three times higher than the values in the NC. In a study conducted in Finland for the emissions of different kind of masonry heaters the PM₁ emission factor was between 0.6 and 1.6 g kg⁻¹ (Tissari *et al.* 2007). Those values are lower than the values for the NC and the SC in this study. The emissions were not measured in controlled laboratory conditions as in this study but on the top of the chimney. The difference could partly be explained by different cut-off size, even though different heater design and sampling setup could also have influenced the results. Some of the combustion appliances could also have had a better primary air flow control than in the heater used in this study, which leads to the lower PM emissions. Hedberg *et al.* (2002) reported emission factors between 0.1 and 2.6 g kg⁻¹ for birch wood burned in a soapstone stove. The emission factors in the NC experiments of the present study were roughly similar to the upper end of that range. Potential reasons may be that the operation of the combustion appliances was probably different, including

Table 1. Averaged contributions (%) and standard deviations of F_E of chemically analyzed compounds to gravimetrically determined F_E in NC (Normal, five samples) and contributions of F_E of chemically analyzed compounds to gravimetrically determined F_E in SC (Smouldering 1 and 2, two samples).

Combustion type	POM	WSPOM	EC	Levoglucosan	Ions	Trace elements	Total
Normal ($N=5$)	33 \pm 9	11 \pm 6	32 \pm 5	3.0 \pm 1.2	19 \pm 3	1.3 \pm 0.3	85 \pm 5
Smouldering 1	67	15	27	2	3	0.3	93
Smouldering 2	69	23	22	3	1	0.3	97

the air supply, burn rate control, firebox size and burning temperature. In an another study $PM_{2.5}$ emissions of a catalyst-equipped wood stove were measured using seven types of wood with and without catalyst (Fine *et al.* 2004). In this case, $PM_{2.5}$ emissions ranged from 0.88 to 3.4 g kg⁻¹ wood burned. Here, the variation of the emissions was caused by the different wood types and noncatalytic and catalytic use of the stove. In a study by McDonald *et al.* (2000), where 19 individual wood combustion tests were made, F_E ranged between 2.3 and 9.0 g kg⁻¹ wood burned. McDonald *et al.* (2000) burnt soft- and hardwood in a fireplace with and without grate and in a wood stove. In addition, in the wood-stove experiments fuel load and burn rate were changed. There were two wood-stove experiments that could be compared with the NC and the SC conditions in this study: an experiment using mixed hardwood with high fuel load and low burn rate (SC) and the other with the same fuel type and low fuel load and high burn rate (NC). The emissions in the conditions describing the SC were reported to be 6.1 and 2.5 g kg⁻¹ for the conditions with low fuel load and high burn rate, respectively. These values agree well with the F_E for the SC and the NC in the present study.

The F_E for the PM depend on many factors such as the burn rate, firebox size, stove type, fuel type and fuel moisture content (e.g. McDon-

ald *et al.* 2000, Fine *et al.* 2004, Johansson *et al.* 2004). Thus, it is difficult to specify individual reasons for the variations in the emission rates between different studies.

Particulate organic matter and elemental carbon

The masonry heater used in this study is a common heater type in Finland and was estimated to represent well current residential wood combustion emissions. Burning of wood was much better in the NC when compared with the SC, but it was still to a certain extent incomplete because the control of the primary air supply was insufficient. This was seen in connection to the significant emissions of particulate organic matter (POM) and EC, which was a consequence of e.g. insufficient air supply. The OC converted into POM (including WSPOM and MA components) was the main component in both combustion types. Another abundant component was EC. The value of F_E for POM in the NC was, on average (\pm SD), 0.9 \pm 0.3 g kg⁻¹, while the corresponding values in the two SC experiments were approximately six to seven times higher (5.8 and 6.2 g kg⁻¹). POM comprised about 30% of the NC and 70% of the SC emissions (Table 1), when compared with the total values of F_E determined gravimetrically. According to Reid

Table 2. The value of F_E (g kg⁻¹ wood burned) (avg. \pm SD) of gravimetrically determined $PM_{2.5}$ and analyzed chemical compounds in NC (Normal, five samples) and SC (Smouldering 1 and 2, two samples).

Compound	Combustion type		
	Normal	Smouldering 1	Smouldering 2
$PM_{2.5}$	2.7 \pm 0.4	8.7	9.0
POM	0.9 \pm 0.3	5.8	6.2
WSPOM	0.3 \pm 0.2	1.3	2.1
MA	0.11 \pm 0.05	0.27	0.45
Levoglucozan	0.08 \pm 0.04	0.18	0.27
Mannosan	0.02 \pm 0.006	0.04	0.11
Galactosan	0.01 \pm 0.005	0.05	0.07
EC	0.9 \pm 0.2	2.3	2.0
Ions	0.50 \pm 0.06	0.24	0.13
K ⁺	0.29 \pm 0.03	0.15	0.08
SO ₄ ²⁻	0.14 \pm 0.02	0.06	0.03
Trace elements	0.036 \pm 0.005	0.028	0.025
Zn	0.033 \pm 0.005	0.026	0.024

et al. (2005), biomass combustion particles are composed of about 50%–60% of organic carbon (OC) depending of the type of the fuel and combustion.

The contribution of WSOC to OC was on average (\pm SD) 30% \pm 11% in the NC, whereas in the SC it was 20% and 30%. The value of F_E for WSPOM in the NC and SC were 0.3 \pm 0.2 and approximately 1.3 and 2.1 g kg⁻¹ wood burned, respectively (Table 2). The contribution of WSOC to OC in the ambient air during episodes of biomass combustion aerosol (wildfire or residential wood burning) has been determined to be approximately 40%–80%, with a large fraction of secondary organic species (Decesari *et al.* 2001, Jaffrezo *et al.* 2005, Timonen *et al.* 2008). The values in the present study were clearly lower probably due to the fact that the emissions were measured right after the combustion process and the aging of the aerosol was minimal.

In the present study, the fraction of EC from the total emissions was 32% \pm 5% in the NC. For the SC, these fractions were 27 and 22%. Even though the fraction of EC was higher in the NC, the value of F_E for EC in the SC (2.3 and 2.0 g kg⁻¹ wood burned) was more than twice that in the NC (0.9 \pm 0.2 g kg⁻¹ wood burned) conditions (Table 2).

The EC-to-OC ratio is one way to characterize the source of atmospheric particulate emissions. A low ratio usually indicates biomass burning (e.g. Khalil and Rasmussen 2003). Here, the EC-to-OC ratio was on average 1.7 \pm 0.6 in the NC, whereas the corresponding values in the SC experiments were 0.60 and 0.52. This difference can be explained by the lower combustion temperature and inadequate air supply in the SC experiments, which led to incomplete oxidation of organic species and soot and higher emissions of particulate organics and elemental carbon.

This is consistent with the study by Khalil and Rasmussen (2003). They compared values of F_E at low and high combustion temperatures, which can be compared with the normal and smouldering combustions of our study. Khalil and Rasmussen (2003) measured EC-to-OC ratios that were approximately 1.4 and 0.08 at high and low burning temperatures, respectively. The difference between the EC-to-OC ratios in the two conditions in this study was not as evident as by Khalil and Rasmussen (2003), but the behaviour was comparable.

Levoglucosan

Levoglucosan comprised approximately 3% of the total PM_{2.5} emissions in the NC and 2%–3% in the SC when the contribution of the total MA to the PM_{2.5} was 4% in the NC and 3%–5% in the SC. (Table 1). The values of F_E for levoglucosan in the SC were approximately two to three times higher (0.18 and 0.27 g kg⁻¹ wood burned) than in the NC (0.08 \pm 0.04 g kg⁻¹ wood burned) (Table 2). Levoglucosan comprised 74% \pm 4% and 66% and 59% of the total MA in the NC and the SC conditions, respectively (Table 3). The average ratio of F_E for levoglucosan emissions between the NC and SC conditions was approximately 0.4. This agrees quite well with the results of Engling *et al.* (2006) who observed that levoglucosan emissions for ponderosa pine were approximately two times higher in the smouldering phase (539 mg⁻¹ OC) of the combustion when compared with the flaming phase (248 μ g mg⁻¹ OC). However, the experiments in this study and those of Engling *et al.* (2006) were not completely similar. In the present study, two different types of combustion were compared instead of the two phases (flaming and

Table 3. Average percentage contribution and standard deviation of individual monosaccharide anhydrides to the total MA in NC (Normal), and percentage contribution of individual monosaccharide anhydrides to the total MA in SC (Smouldering 1 and 2).

Combustion type	Levoglucosan/MA	Galactosan/MA	Mannosan/MA
Normal	74 \pm 4	10 \pm 1	15 \pm 3
Smouldering 1	66	17	17
Smouldering 2	59	16	25

smoldering) of one combustion. In addition, the levoglucosan F_E was reported to vary widely depending on a biomass fuel type. For example, emission factors of different types of pine have been found to vary largely, between 0.1 and 1 g kg⁻¹ wood burned (e.g. Fine *et al.* 2002, Fine *et al.* 2004, Iinuma *et al.* 2007). For a comparison, the levoglucosan emissions of German peat, a completely different type of biomass fuel, have been measured to be approximately 5 g kg⁻¹ in laboratory conditions (Iinuma *et al.* 2007).

The ratio of the OC-to-carbon content of levoglucosan was approximately 16 in the NC and 40 in the SC. In the previous studies of Fine *et al.* (2002, 2004), the OC-to-levoglucosan carbon ratios in wood stove studies using different types of firewood ranged from approximately 3 to 30. The results based on the ambient air measurements show clearly larger OC-to-levoglucosan carbon ratios. For instance, according to the observations made in Ghent, Belgium (Zdráhal *et al.* 2002), this ratio was 66 for winter air masses influenced by wood combustion. During the summer season, this ratio increased to approximately 460.

The levoglucosan-to-OC or OC-to-levoglucosan ratio has also been used for deriving the amount of OC from wood or biomass combustion in ambient aerosol (Szidat *et al.* 2006, Puxbaum *et al.* 2007). In the previous investigations, the contribution of the biomass combustion OC to the total ambient OC was estimated by either dividing or multiplying the ambient levoglucosan concentration by the levoglucosan-to-OC or OC-to-levoglucosan ratio based on the data from studies where levoglucosan and OC were determined from the different wood combustion appliances using varying firewood types (e.g. Schauer *et al.* 2001, Fine *et al.* 2002, 2004). Szidat *et al.* (2006) used the value of 0.15 ± 0.09 for the ratio of levoglucosan-to-OC based on the average value of many investigations. The OC-to-levoglucosan ratio of 7.35 based on the emissions from a fireplace using hardwood as firewood (Fine *et al.* 2002) was estimated to hold for conditions, in which a mixture of hard and softwood are used for domestic heating (Puxbaum *et al.* 2007). Results of present study could also be used for a rough assessment of the contribution of particulate OC from residential wood

combustion to total particulate OC in the ambient air. The levoglucosan-to-OC ratio varied in the ranges 0.05–0.09 and 0.02–0.03 for the NC and SC conditions, respectively. The inverse ratios for the NC and SC were in the ranges 8–15 and 33–47, respectively. These ratios differed from the ones used in the studies of Szidat *et al.* (2006) and Puxbaum *et al.* (2007). According to this measurement the contribution of levoglucosan-to-OC vary clearly between the NC and SC conditions and even between the two measurements in the same conditions. In addition, other investigations have shown large differences in levoglucosan and OC concentrations depending from the wood and wood combustion appliance type. Thus, the uncertainty of the source assessment based on the levoglucosan and OC results is quite large. However, rough source assessments could be done based on the contributions of this and other studies. The data of this study would fit best for the source assessment in Finland or in the environment were same kind of combustion appliances and wood types are used.

Major ions

During a combustion process, vaporization of inorganic species to the flue gas depends strongly on the vapour pressure of the fuel species and combustion temperature. As the flue gas cools down, evaporated inorganic species, such as ions, contribute to the formation of particles by homogenous nucleation and subsequent condensation (e.g. Rissler *et al.* 2005). Thus, while the vaporization increases due to a rise in temperature also the inorganic particulate matter emissions increase. The results from the present investigation are consistent with this fact.

Ions analyzed from the PTFE filters of the VI samplers contributed to about 20% of the total PM_{2.5} emissions in the NC but only 1%–3% in the SC (Table 1). On average, the values of F_E for ions were approximately 2 to 4 times for the NC (0.50 ± 0.06 g kg⁻¹ wood burned) compared with those for the SC (0.24 and 0.13 g kg⁻¹ wood burned) (Table 2). The most abundant ion was potassium (K⁺) that contributed to 98% of the total cation emissions and 60% of all the analyzed

ions in both combustion conditions. The significance of K^+ as a tracer of woodsmoke emissions has been seen also in atmospheric measurements. According to Saarikoski *et al.* (2008b), the mass concentration of K^+ was approximately seven times higher during a wildfire episode when compared with the normal urban background concentrations. In the present emission study, the fraction of K^+ in total fine particle emissions was similar to the sum of analyzed ions: it comprised 11% and 1% of all fine particle emissions in the NC and SC, respectively. In wood stove tests made by Fine *et al.* (2004), K^+ comprised on average approximately 1% of the $PM_{2.5}$. This fraction is comparable with the present results on the SC but the K^+ fraction in the NC is distinctly higher. On the other hand, observations of K fractions in four Finnish masonry heaters varied between 4% and 20% with an average of 13% (Tissari *et al.* 2007). This agrees well with our findings. In another study, inorganic emissions from wood stove corresponded to the SC conditions in the present study, even though the combustion temperature in the stove was rather high, 260–316 °C (Fine *et al.* 2004). One reason for variations of the results between different studies could be in the analytical methods. In this study, potassium was analyzed as ionic compound by ion chromatography where as in the studies of Fine *et al.* (2004) and Tissari *et al.* (2007) potassium was analyzed as elemental component using X-ray fluorescence and ICP-MS techniques, respectively.

In anions, the most dominant species was sulfate (SO_4^{2-}), contributing to about 60% of the total anion emissions. Chloride (Cl^-) has also been identified as one of the main ions in biomass combustion emissions (McDonald *et al.* 2000). In the present study, the contribution of Cl^- to the total anions was 13% and 20%–25% in the NC and SC, respectively. The contributions of other anions (nitrate, nitrite, oxalate) were smaller than 10%.

Trace elements

The concentrations of some trace elements have been found to increase when atmospheric air masses are polluted by emissions from wood or

other biomass burning. Especially in open biomass burning, elements from the soil on which the burning takes place may be entered into air together with elements associated with the fuel. Components that have been found include K, Si, Zn, Al, S, Cl, Al, Pb, Ni, As, P (e.g. Hedberg *et al.* 2002, Khalil and Rasmussen 2003, Sillanpää *et al.* 2005b). However, the concentrations of most of these elements are strongly influenced also by other sources, especially in urban environments. For example, vehicular, waste burning and other industrial activities contribute the atmospheric concentrations of these elements. In addition, Cl and S may be associated with sea-salt aerosols (Braga *et al.* 2005).

In the present study, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, V and Zn were analyzed using the ICP-MS, whereas K and Cl were measured as ions by the IC. After subtracting blank values of the analyzed substrates, reasonable emission factors were got for Al, Mn, Pb, Fe and Zn. Altogether, the analyzed elements comprised only about 1 percent of the total fine particle mass in the NC (F_E of 0.036 ± 0.005 g kg^{-1} wood burned) and even less in the SC (F_E of 0.028 and 0.025 g kg^{-1} wood burned) (Tables 1 and 2). The fraction of elements, including also some other elemental components than the ones analyzed in this study, has been observed to be around 1% in wood stove studies using different wood types as firewood (Fine *et al.* 2002, Fine *et al.* 2004, Hedberg *et al.* 2002). This is consistent with the present study. On average, Zn contributed to 94% of the analyzed trace elements, while according to Fine *et al.* (2002, 2004) and Hedberg *et al.* (2002) the corresponding fraction was between 70 and 80%. This can partly be explained by some differences in analyzed compounds. Concerning the use of Zn as an atmospheric tracer for biomass burning, it has to be noticed that in addition to biomass burning there are also other sources of Zn, such as coal fly ash from the coal-fired power plants and other industrial activities (Salam *et al.* 2003, Braga *et al.* 2005).

Mass size distribution

The differences in the emission properties between the NC and SC were also reflected in the

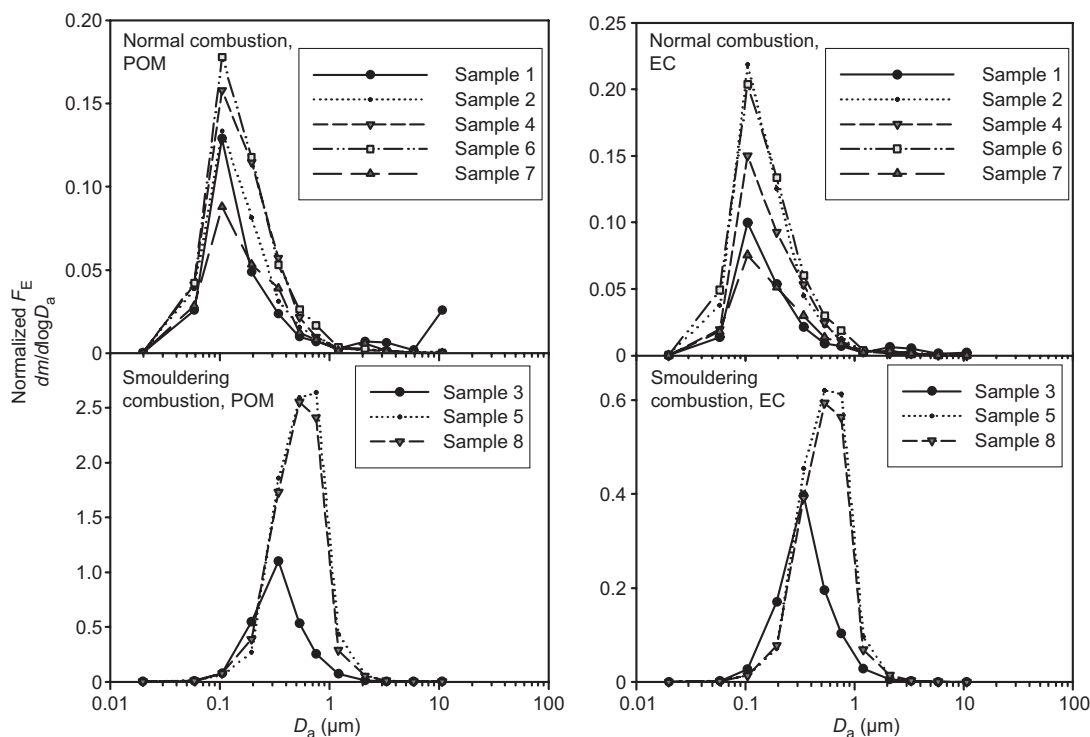


Fig. 2. F_E size distributions of POM and EC normalized by the sum of the analyzed POM and EC for the NC and SC cases.

mass size distributions of chemical compounds analyzed from the SDI samples. The results from all three SC experiments are shown although the sample 5 is not included in the emission calculations (using the VI data). This is because the analyze result of the sample 5 differed clearly from the two other SC measurements probably due to the overloading of the denuders. In the case of the SDI, the gas phase artifact in the samples is not as likely because of the low pressure in the impactor. Gas phase has potential to evaporate already during the sampling. Thus, differences in the mass size distributions probably depend on the variation in the combustion process.

In the emissions from the NC, POM and EC had two or three modes (Fig. 2), with a maximum of the first mode at about 100 nm (aerodynamic diameter). The second mode between 1000 and 1200 nm was quite low. In addition, a small mode was seen at particle size larger than 1.2 μm . In the SC, the shapes of POM and EC distribution were unimodal with a maximum at about 500 nm (Fig. 2).

As the other primary particulate matter species from wood combustion, MA was found mainly in submicrometer particles. The mass size distribution of MA was usually unimodal with a maximum at about 200 nm (aerodynamic diameter) in the NC (Fig. 3). In the SC the shape of the mass size distribution varied between uni- and bimodal, with maxima at approximately 300 or 700 nm. There are a few previous studies on size distributions of particulate MA or levoglucosan (Engling *et al.* 2006, Iinuma *et al.* 2007). Engling *et al.* (2006) found most of the levoglucosan between approximately 0.1–1.0 μm when oak wood was burned in a chamber. This data is quite crude because size-segregation was made by using only five stages and particles below approximately 500 nm were collected on a backup filter. Iinuma *et al.* (2007) determined the contribution of organic carbon mass in MA to the total carbon mass (%) for many biomass fuels. In their study, the highest fraction of MA was observed in particles between 0.05 and 0.14 μm for pine without needles and spruce with green

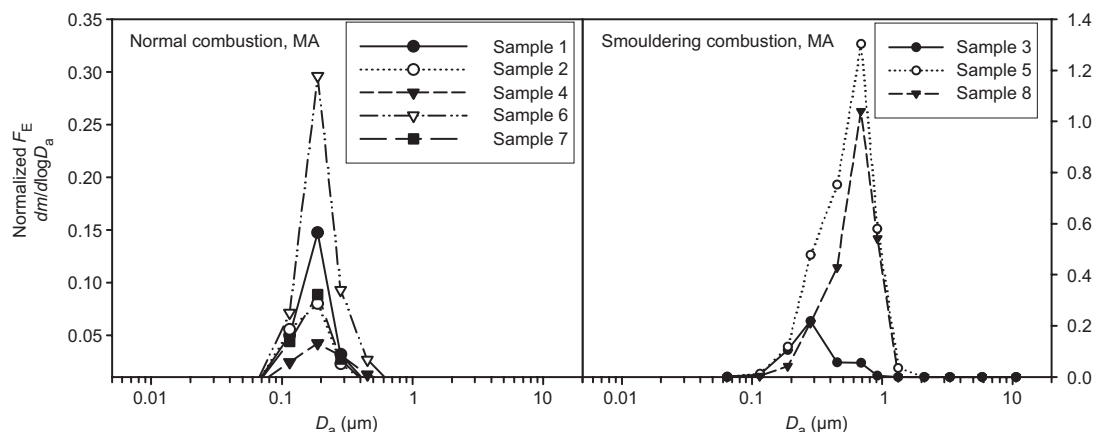


Fig. 3. F_E size distributions of MA normalized by the sum of the F_E of the analyzed MA and ions for the NC and SC cases.

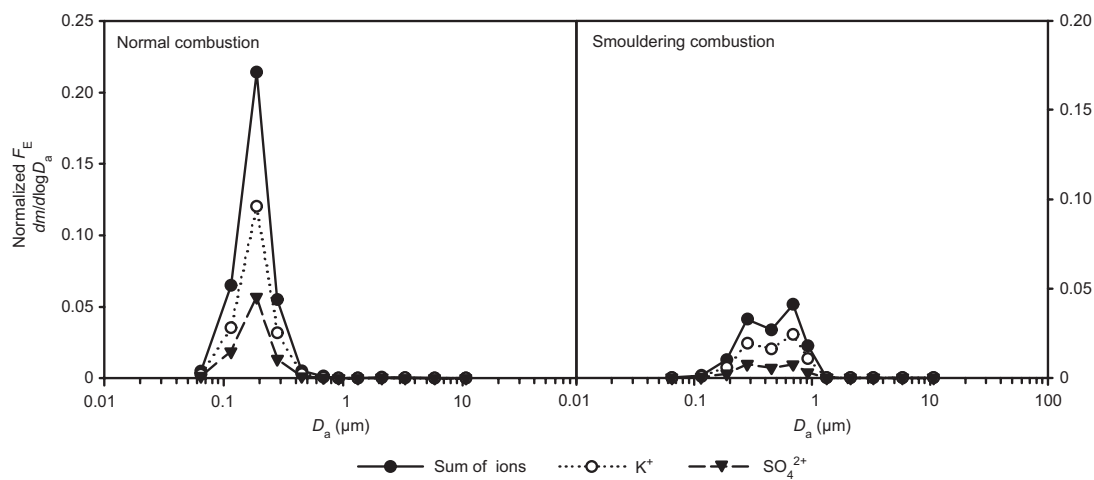


Fig. 4. F_E size distributions of the major cation (K^+), anion (SO_4^{2-}) and sum of ions in one NC and SC case. The distributions are normalized by the sum of the F_E of the analyzed MA and ions. Examples are from the combustion samples 1 and 8.

needles. This maximum is slightly smaller than 200 nm measured in the case of the NC in this study. According to Iinuma *et al.* (2007), the MA fraction was the highest in particles between 0.42 and 1.2 μm when using pine with green needles as firewood, which is consistent with the SC case in our study.

Combustion conditions also affected the mass size distributions of ionic components. The type of burning had the same influence on all major components: ion emissions peaked at about 200 nm in the NC (Fig. 4). The shape of the distribution varied more in smouldering combustion

where either uni- or bimodal with a maximum at 200 and 700 nm was measured (Fig. 4).

Conclusions and implications

The present study showed that fine particle emissions depend strongly on combustion air supply as well as the log and batch size. Poor operation in log-wood combustion lead to a low burning temperature and insufficient oxidation of the flue gases causing smouldering combustion. Smouldering combustion increased particulate

emissions significantly. Three times higher total fine particle emissions were measured when the conditions varied from normal to smouldering combustion.

POM, EC, K⁺ and levoglucosan was found to be typical chemical components of wood combustion. The POM-to-PM_{2.5} ratio was clearly higher in the SC when compared with that in the NC conditions. Better combustion air supply and a higher combustion temperature in the NC decreased the release of OC as compared with EC. The fraction of WSOC in OC was independent of the combustion type. Levoglucosan emissions were from two to three-fold higher in the SC. Contrary to carbonaceous species, emissions of ionic species were clearly higher in the NC when compared with the smouldering conditions. The values of F_E for trace elements were small and consisted mainly of zinc.

The EC and POM mass size distributions had, on average, mass modal diameter at lower particle sizes in the NC compared with that in the smouldering conditions. The MA mass size distributions were quite narrow in both the burning conditions, but the mass modal diameter was larger in the SC. For ions, the average mass size distributions over the combustion cycle were unimodal in the NC and bimodal in the SC.

According to the results of this study, the POM-to-PM_{2.5} and EC-to-OC ratios are good indicators to describe differences in combustion conditions. Variations in the combustion temperature can also be seen in particulate emissions of ionic compounds, as was seen in increasing emissions of analyzed ions in the NC conditions. The major ion and element were potassium and zinc, respectively. Levoglucosan emissions showed also differences between the NC and SC conditions. Since levoglucosan is released only when wood is burned, it is a good tracer of wood smoke emissions in the ambient air. Potassium and zinc as wood smoke tracers may be limited because they have also other sources. Mass size distributions of different chemical compounds seem also to be characteristic for different combustion conditions.

The number of the samples in this study was quite small, but the measured deviations in the repeated tests were not significant. Therefore the present chemical characterization of fine parti-

cle emissions from the two wood combustion conditions can be utilized as one reference when different combustion conditions, different heating appliances and different biomass fuels are compared. It also shows the importance to promote proper operational practices in wood combustion. Despite the small number of tests, the results of this study enable a rough assessment of the contribution of OC from the residential wood combustion in ambient air.

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